

SEPARATION OF CARBON MONOXIDE AND CARBON DIOXIDE FOR MARS ISRU

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The atmosphere of Mars has many resources that can be processed to produce things such as oxygen, fuel, buffer gas, and water for support of human exploration missions. Successful manipulation of these resources is crucial for safe, cost-effective, and self-sufficient long-term human exploration of Mars. In our research, we are developing enabling technologies that require fundamental knowledge of adsorptive gas storage and separation processes. In particular, we are designing and constructing an innovative, low mass, low power separation device to recover carbon dioxide and carbon monoxide for Mars ISRU (in-situ resource utilization). The technology has broad implications for gas storage and separations for gas-solid systems that are ideally suited for reduced gravitational environments. This paper describes our separation process design and experimental procedures and reports results for the separation of CO₂ and CO by a four-step adsorption cycle.

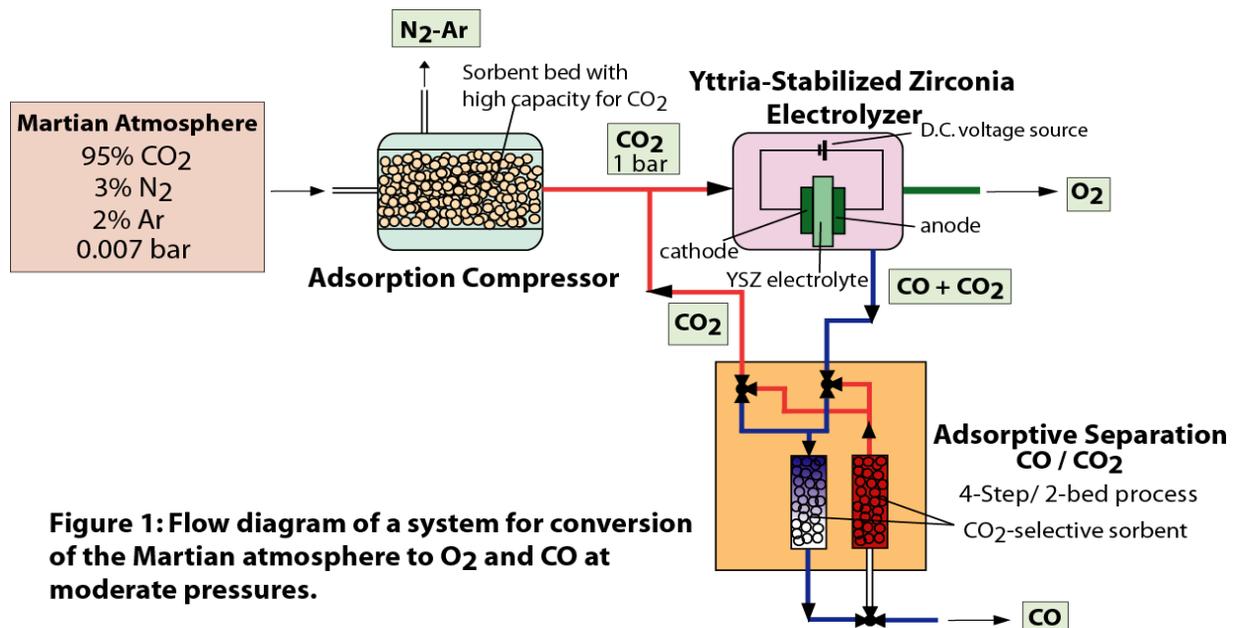


Figure 1: Flow diagram of a system for conversion of the Martian atmosphere to O₂ and CO at moderate pressures.

As illustrated in Figure 1, this work comprises one-third of an overall process for producing O₂ and CO at moderate pressures from the Martian atmosphere. An adsorption compressor, developed by Dr. John E. Finn at NASA Ames Research Center, adsorbs CO₂ from the atmosphere and compresses it to a pressure of 1 bar. The CO₂ is then passed to a solid oxide electrolysis cell developed by K. R. Sridhar at the University of Arizona. This electrolysis cell makes use of yttria-stabilized zirconia to produce oxygen from the compressed planetary CO₂ and will then reject CO and unreacted CO₂ in a separate stream. The efficiency of the oxygen-production process is greatly improved if the unreacted CO₂ is separated and recycled back into the feed stream. The separation will also have a positive impact on the mass of the adsorption compressor because less CO₂ will be needed from the atmosphere. Additionally, the CO by-product is a valuable fuel for space exploration and habitation, with applications from fuel cells to production of hydrocarbons and plastics.

Our separation device contains a CO₂-selective sorbent such that when the mixture is fed from the electrolyzer, CO₂ adsorbs and CO passes through the bed with minimal adsorption. The cycle is illustrated by Figure 2. The mixture is fed at a temperature of 273K. When the bed reaches capacity, it is isolated and heated with no flow at 398K to desorb the CO₂. CO₂ at high pressure is then allowed to pass to a storage tank at sufficient pressure to feed the electrolyzer. The bed is then cooled back to 273K prior to returning to the feed step. We envision a two-bed system in which one bed is onstream for the feed step while the other is undergoing regeneration and blowdown of CO₂.

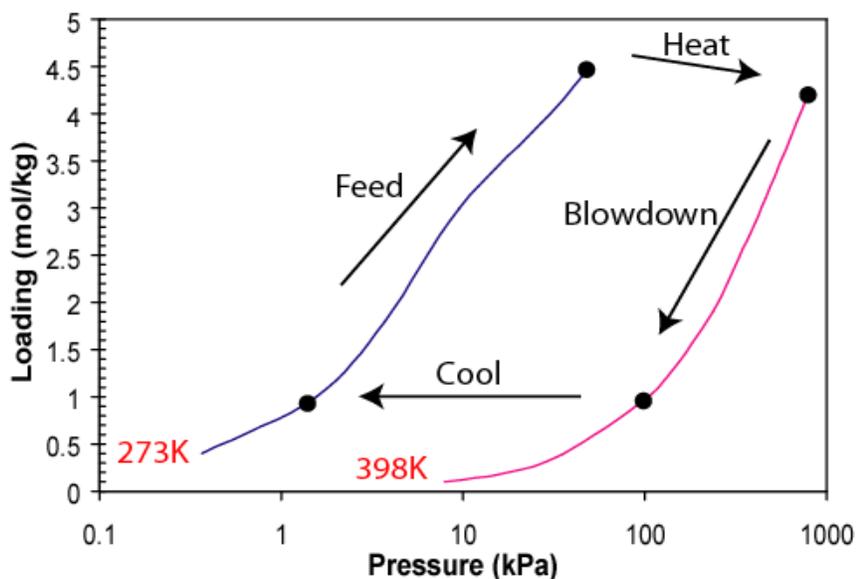


Figure 2: Depiction of four-step adsorption cycle between CO₂ adsorption isotherms on NaY zeolite.

We have a working prototype and have performed the proposed cycle. We have developed process models and are continuing to optimize the separation. All of these results will be discussed.



Separation of Carbon Monoxide and Carbon Dioxide for Mars ISRU

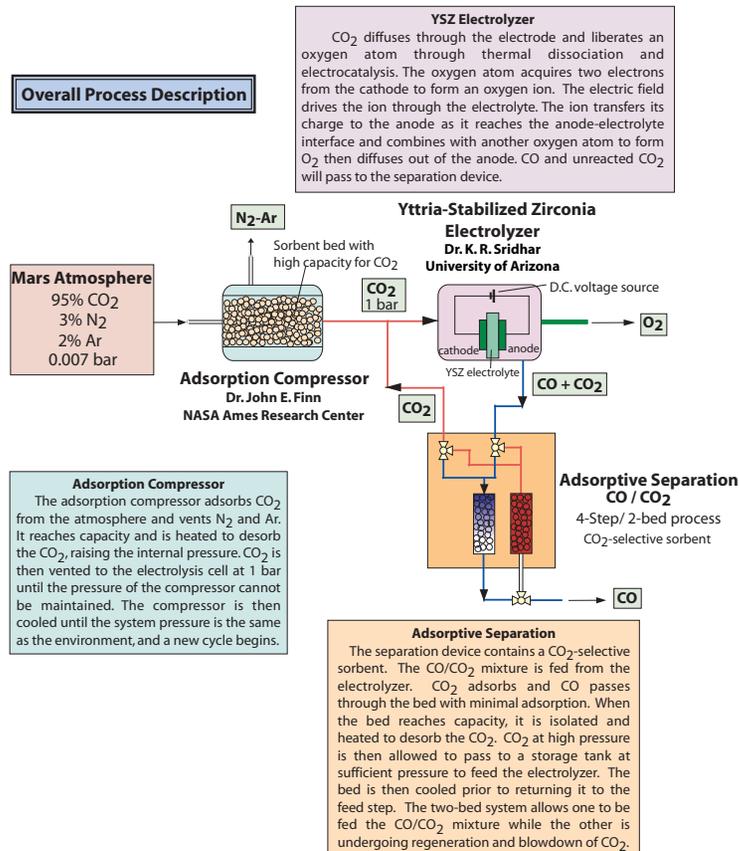
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ABSTRACT

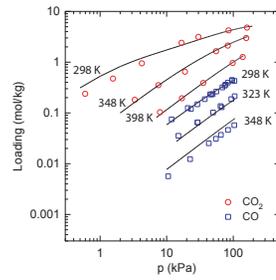
The atmosphere of Mars has many resources that can be processed to produce useful materials like oxygen, fuel, buffer gas, and water for support of human exploration missions. In this research, we are designing and constructing an innovative, low mass, low power separation device to recover carbon dioxide and carbon monoxide for Mars ISRU (in-situ resource utilization). The separation is accomplished by a four-step adsorption process. The technology has broad implications for gas storage and separations for gas-solid systems that are ideally suited for reduced gravitational environments.

Overall Process Description



Adsorption Compressor
The adsorption compressor adsorbs CO₂ from the atmosphere and vents N₂ and Ar. It reaches capacity and is heated to desorb the CO₂, raising the internal pressure. CO₂ is then vented to the electrolysis cell at 1 bar until the pressure of the compressor cannot be maintained. The compressor is then cooled until the system pressure is the same as the environment, and a new cycle begins.

Adsorption Equilibria: Measurements and Modeling

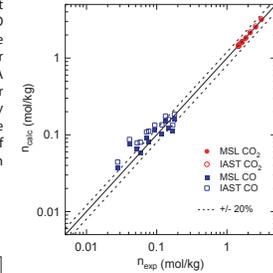


Pure-component adsorption isotherms on NaY zeolite. Lines are multisite Langmuir fits.

We have measured both pure-component and binary adsorption equilibrium data for CO and CO₂ on NaY zeolite molecular sieve. These data and their description are critical for designing an adsorptive separation process. A temperature-dependent multisite Langmuir equation has been used to model successfully all adsorption equilibria data, both pure component and binary, using only one set of parameters. This model can be used easily in non-isothermal fixed-bed simulations.

$$n_i = \frac{m_i b_i P_i}{(1 + b_i P_i + b_j P_j)} + \frac{m_d d_i P_i}{(1 + d_i P_i + d_j P_j)}$$

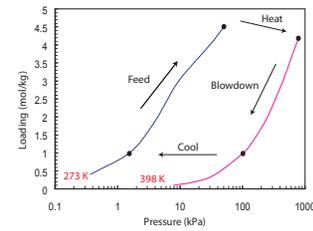
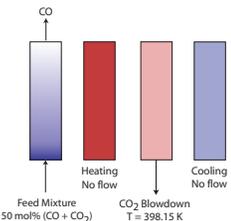
$$b_i = b_{i0} \exp\left[\frac{q_{i0}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad d_i = d_{i0} \exp\left[\frac{q_{d0}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$



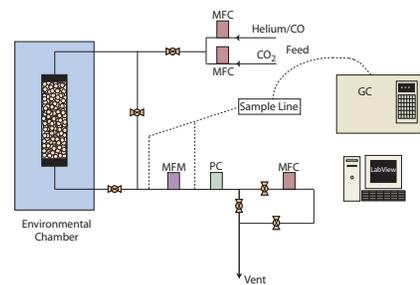
Comparison of binary adsorption data with values calculated from multisite Langmuir and IAST

4-step Adsorption Cycle

Our separation device contains a CO₂-selective sorbent such that when the mixture is fed from the electrolyzer, CO₂ adsorbs and CO passes through the bed with minimal adsorption. The mixture is fed at a temperature of 273 K. When the bed reaches capacity, it is isolated and heated with no flow at 398 K to desorb the CO₂. CO₂ at high pressure is then allowed to pass to a storage tank at sufficient pressure to feed the electrolyzer. The bed is then cooled back to 273 K prior to returning to the feed step. We envision a two-bed system in which one bed is onstream for the feed step while the other is undergoing regeneration and blowdown of CO₂.

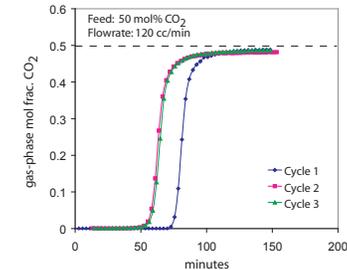


Experimental Apparatus



The device is heated or cooled by an environmental chamber. Mass flow controllers allow constant feed of the mixture at prescribed rates. A mass flow meter measures the product flow and a pressure controller maintains downstream pressure at setpoint. An additional mass flow controller is used to control the flow of CO₂ during blowdown. A gas chromatograph allows analysis of the composition of the product stream. The process is automated by National Instrument's LabView software.

CO₂ Breakthrough Curve



CO₂ begins to breakthrough the bed around 1 hour and 10 minutes after the feed step has begun for the first cycle. For the subsequent 2 cycles, CO₂ begins to breakthrough earlier after a feed duration of approximately 1 hour. Before CO₂ breakthrough, we are producing mostly pure helium with small traces of CO₂. We expect similar behavior for a mixture of CO and CO₂ based on binary adsorption measurements.